

THERMOPLASTICALLY PROCESSABLE GRAFT POLYMERS
[Thermoplastisch verarbeitbare Pfropfpolymeren]

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b. 1 + additives

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THERMOPLASTICALLY PROCESSABLE GRAFT POLYMERS

[Thermoplastisch verarbeitbare Pfropfpolymerie]

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The invention relates to thermoplastically processable graft polymers which have a low number of amino acid units grafted to a central structural unit, to a method for its manufacture, and to its use.

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DE 19 05 452 A2 discloses extremely high-molecular-weight polyamide graft polymers for the manufacture of threads and films with a decreased sensitivity to humidity, so that, as a result, all the mechanical properties that are negatively influenced by water uptake are improved. Starting with olefin polymers forming the base chain and having a molecular weight of 10,000-300,000 g/mol, with 50-350 side chains, the patent describes the manufacture of polymers with molecular weights of 300,000-800,000 g/mol, which, however, are not suitable for processing by injection molding.

DE 38 19 427 A1 describes multiply branched pure polyamide structures, and in it the state of the art regarding the manufacture of branched polyamides using polyfunctional carboxylic acids and amines is presented in detail.

If one wants to avoid crosslinking events during the hydrolytic polymerization, then amino acids and/or lactams can be used as base monomers. If one wants to prepare polymers in a targeted way with more than 3 polymer chains per molecule, polyfunctional carboxylic acids and amides must generally be combined with each other while strictly restricting the rules of stoichiometry.

If the stoichiometric proportions are not respected exactly, the polymer properties can change drastically, and there is already a risk of crosslinking in the polycondensation vessel. In addition, tri- and multifunctional carboxylic acids, such as trimesic acid used in the conventional manner, are not easily produced and are expensive. Theoretical examinations concerning the rheological behavior of centrally branched polyamides with amino acids as monomers are described in "Journal of the American Chemical Society" 70 (1948) on pages 2709-2718. However, the polycarboxylic acids described therein are accessible only with difficulty, so that this publication is limited particularly to rheological studies conducted on polymer solutions and small melted samples.

The invention is based on the problem of creating new polymers with very good thermoplastic processing properties, and a large range of variations of their properties and application fields, where the properties are like those of the known

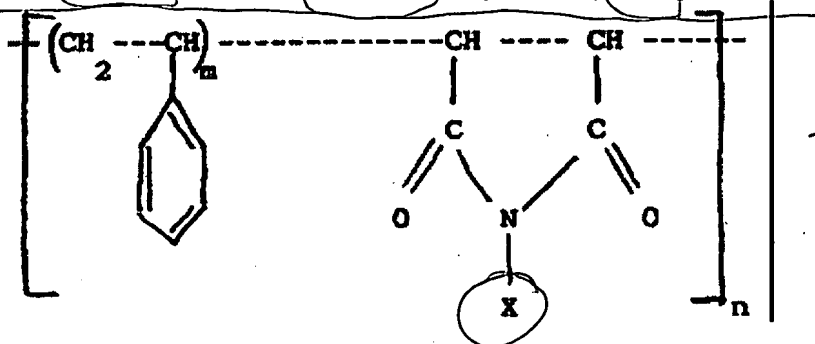
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polyamino acid polyamides in terms of their basic behavior, but can be manufactured without the use of a complicated branching regulation-system.

This problem is solved by the graft polymers of Claim 1.

Claims 2-13 contain preferred embodiments of the graft polymers according to the invention, and Claim 14 presents their use for the manufacture of mold parts.

Accordingly, the invention relates to new, thermoplastically processable polymers, which possess a structure based on styrene-maleinimide base structural units, as well as grafted polymer chains of polyamino acids. The base structure of maleinimide with styrene units is constructed in such a manner that, according to the formula I indicated in Claim 1, in each case 1-5, preferably 1-3, and particularly 1-2, styrene units are linked with a maleinimide unit, where the polymerization degree of such styrene-maleinimide units is approximately 3-15, preferably 4-8, and particularly 5-7, and where the molecular weight of these units is 600-9000, preferably 1200-6000, and particularly 2000 g/mol.



where
m = 1-5 and
n = 3-15.

In the formula I, m and n are, of course, statistical means. At position X, the grafting with polyamino acid chains occurs, with n equal to 3-15, and preferably 4-8, and particularly 5-7, per molecule of the graft polymer. The result is, with average polymerization degrees of the polyamino acid chains, 30-70 graft polymers in the molecular weight range of 10,000-100,000 g/mol.

This molecule structure, in contrast to a comb-like structure with a very large number of polyamino acid side chains, ensures an excellent melt flow capacity, still maintaining good mechanical properties which is clear improvement over chain molecules with similar molecular weight.

The graft polymers according to the invention can be processed in an excellent way thermoplastically, particularly in the injection molding method. In the process, they are characterized particularly by the fact that even complicated parts with thin wall thicknesses can be produced while achieving an excellent surface.

Many properties of the new polymers according to the invention can be predetermined by the targeted choice of the monomers for the polymer chains in a broad range. For example, if caprolactam is chosen as monomer, and the weight proportion of the central styrene-maleinimide unit is less than approximately 50 wt%, then the graft polymers present largely the properties of polyamide 6. If amino undecanoic acid or amino lauric acid is chosen as monomer for the polymer chain, then the polymer properties resemble the properties of the homopolyamides polyamide-11 and polyamide-12. If copolyamides are to be produced from mixtures of these monomers, then, from the mixing ratio of the monomers and the weight portion of the base structural unit, additional polymer properties, such as the melting point, crystallization capacity, water uptake, resistance to chemicals, hardness, etc., can be influenced in a targeted manner.

The number of styrene-maleinimide units, as well as the ratio of styrene to maleic acid anhydride, which is expressed as m, of the styrene-maleic acid anhydride mixture (SMA) used for the manufacture of the graft polymers, also influence the polymer properties disadvantageously. If the ratio m is close to 1, and n is 3-15, preferably 4-8, and particularly 5-7, then particularly preferred graft polymers are produced with a largely centrally branched polymer structure. For example, in comparison to linear polyamide made of the same polyamide components (for example, 6-lactam), they possess, while having a similar molecular weight, clearly improved processing properties, because the polyamide melt flows clearly better under a load.

The graft polymers according to the invention consist of a central styrene-maleinimide base structure unit with polyamino acid chains grafted on them, and carrying carboxyl end groups, which in turn can be reacted at least partially with primary amines. The polymer composition can contain linear polyamino acid molecules in quantities of 0.1-15 wt%. The SMA resin used for the manufacture of the base structure unit preferably has a structure in which 1-5 styrene units are connected with a maleic acid anhydride unit (MA), where the number of the styrene-maleic acid anhydride units (SMA) is

3-15. It is particularly preferred to use SMA oligomers with a low number, preferably 1-3, particularly 1-2, of styrene units per MA, and a number of SMA units of 4-8, and particularly 5-7.

It is preferred to use amino acids and/or lactams for the manufacture of the polyamino acid chains. In particular, caprolactam, oenantholactam and laurilactam, as well as the corresponding amino carboxylic acids, are used, such as ω -aminoundecanoic acid, ω -aminododecanoic acid, and 4-aminomethylbenzoic acid. Depending on the desired product properties, the monomer or mixtures thereof can be used. If a mixture of SMA resin and monomers is used for the polymer manufacture, for example, aminoundecanoic acid, then the graft polymers have COOH end groups.

If their concentration is to be reduced, a primary amine can be added to the monomer mixture. Depending on the concentration of added primary amine, the number of the carboxylic end groups is reduced in a targeted way in the process. If a quantity of primary amine is added which is greater than that which corresponds to the polyamino acid chains growing from the SMA center, then the primary amine itself acts as a chain regulator, and linear polyamino acid chains are produced in the polymer melt to a degree corresponding to the weight proportion.

The primary amine is therefore used advantageously at a maximum concentration which corresponds to the following formula:

$$C_A \leq C_{SMA} \eta + 50 \mu\text{mol/g polymer}$$

Wherein:

C_A stands for the concentration of the primary amine,

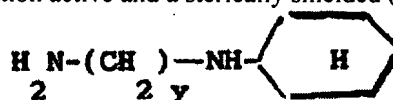
C_{SMA} stands for the concentration of the SMA resin,

each expressed in $\mu\text{mol/g}$ of the produced polymer composition, and

η is the number of MA units of the SMA resin.

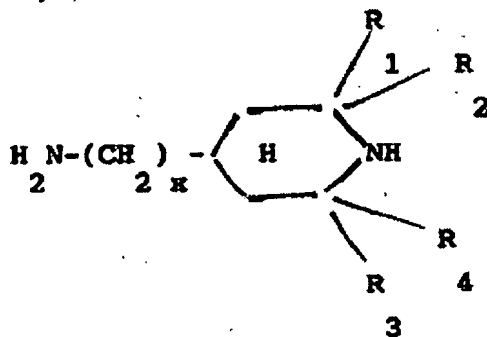
As primary amines, it is preferred to use aliphatic amines having particularly 3-18 carbon atoms, which are preferably linear, such as tridecylamine, cycloaliphatic amines with 6-18 carbon atoms, such as cyclohexylamine, and aromatic amines with 6-18 carbon atoms, such as benzylamine.

Furthermore, amines having a condensation active and a sterically shielded (hindered) amino group can be used, such as:



(III)

where y stands for 2-12, and particularly 3, and:



(IV)

where x stands for 0-12, and R_1, R_2, R_3 and R_4 are identical or different alkyl groups with 1-4 carbon atoms, particularly methyl groups.

If the carboxyl end groups of the graft polymers are to be kept, or if additional linear polyamino acid chains are desired, then one can add to the polymerizing polymer mixtures a mono- and/or dicarboxylic acid in a chain length-regulating proportion. Monocarboxylic acids that can be used are aliphatic monocarboxylic acids with 2-18 carbon atoms, such as acetic acid, aromatic monocarboxylic acids with 7-18 carbon atoms, such as benzoic acid, aliphatic monocarboxylic acids with 7-18 carbon atoms, as well as alicyclic monocarboxylic acids with 7-18 carbon atoms. As dicarboxylic acids, the following are mentioned: aliphatic dicarboxylic acids with 2-18 carbon atoms, such as adipic acid; aromatic dicarboxylic acids with 8-18 carbon atoms, such as terephthalic acid; aliphatic [dicarboxylic acids] with 9-18 carbon atoms as well as alicyclic [dicarboxylic acids] with 8-18 carbon atoms.

The manufacture of the graft polymers according to the invention is carried out preferably in such a way that an SMA resin is added to the amino acids and lactams or mixtures thereof, which is/are used as monomers, and the mixture is melted and polymerized hydrolytically in a manner which itself is known.

If the monomers are exclusively amino acids, then, after the melting, a pure polycondensation reaction occurs, and the amino groups of the amino acids react with the MA groups of the SMA resin with the formation of the imide structure, while the attachment by condensation of the growing polyamino acid chains occurs via the carboxyl groups.

If a lactam is used or used simultaneously, then, in an advantageous manner, a pressurized phase is used beforehand for opening the lactam ring. This measure is advantageous particularly if a laurin lactam is used. The conditions for such a pressurized phase correspond to those that are used for the manufacture of polyamide-12. Advantageously, the reaction temperatures are kept at 150°C and higher, whereby reaction temperatures of preferably 290°C should not be exceeded.

If monofunctional compounds, particularly primary amines, are used simultaneously in a chain or end group-regulating mol portion, then the polycondensation in the end phase is delayed, because the growing chain segments have to recombine with each other. In this case, the condensation time also has to be increased, and/or the temperature increased, and a vacuum is applied to advantage. After reaching the desired molecular weight, the melt can be drawn off as a strand, and the strand can be granulated after solidification in the usual manner.

Processing tests using polymers according to the invention, for example, by injection molding, show that very good flowing melts are obtained under load, and thin-walled and complicated parts can be manufactured easily. Because of their high concentration of end groups, which are preferably carboxyl groups, compared to linear polyamide, for example, such products are suitable, for example, as melt adhesives, where the melting point can be adapted in a targeted manner to the practical requirements by the specific choice of the monomer mixture. They are all suitable for filling and reinforcing minerals and glass fibers, if they are, as is done conventionally today and is part of the state of the art, coated with amine silane. If formulations with -NHR chain ends (R = alkyl with 3-18 carbon atoms) are manufactured in a targeted manner, then they are also suitable for silane crosslinking, for example, by the method described in CH-PS 663 621, and very high rigidities can be obtained because of their potentially high concentration of crosslinkage-active -NHR chain ends.

The graft polymers according to the invention can also be modified with any conventional polymer additives, such as fillers and reinforcers, according to the state of the art. Examples of such materials are: stabilizers (against heat, light and radiation effects, as well as against degradation during the processing), dyes and pigments, softeners, minerals and glass beads, fibrous additives, for example, made of glass, carbon and minerals.

The following examples explain the invention without limiting it.

The following compounds are used as monomers:

Compound	Abbreviation
Caprolactam	CL
ω -Aminocaproic acid	ACS
ω -Aminolauric acid	ALS

The imide forming components are styrene-maleic acid anhydride resin (SMA) (products which are available commercially under the trade names SMA Resins® with type designations 1000, 2000 and 3000 from Arco Chemicals, Channelview, Texas, USA).

Table 1 characterizes the properties of different available SMA resins:

TABLE 1

SMA type	Mn (g/mol)	Melting range/°C	Acid number	Number of MA units per SMA molecule, as statistical mean
1000	1600	150-170	480	6.9
2000	1700	140-160	350	5.4
3000	1900	115-130	275	4.6

The acid number here gives the quantity of KOH in mg, which is required to neutralize the carboxyl groups of 1 g SMA resin.

In the graft polymers according to the invention, which contain amino end groups, 3-amino-1-cyclohexylaminopropane (Laromin C-252 R from the company BASF) is added to the monomers.

Examples 1-7

On the laboratory scale, the starting monomers and the SMA resin, as well as optionally the Laromin C-252, are weighed with approximately 1-3 mL water in a condensation pipe, and melted at 200-220°C under a continuous N₂ stream. After 1 h, the temperature is increased 250°C and 270°C, respectively, and condensed for 4-6 h.

The recipes and test conditions in each case can be taken from Table 2. The result consists of approximately 70 g graft polymers, whose properties for characterization are also listed in Table 2. Using these laboratory batches which were run without pressure application, one can see that, as a result of the ratio of the amino lauric acid to the SMA resin, the solution viscosity, the melt viscosity, and the COOH group concentration are established. Furthermore, one can see that in the examples according to the invention the NH₂ end group concentration is not greater than 7 μ mol/g polymer.

The glass transition temperatures (T_g) and melting points (mp) are measured using the thermo-analysis system 990 (Du Pont). As T_g , the maximum of the melt endotherm was used, and as melting point, the maximum at the beginning of the glass transition was used.

The solution viscosities η_{rel} were determined according to DIN 53 727, where the polymer concentration was 5 mg/mL in m-cresol.

The melt viscosities were measured at 270°C and under a load of 122.6 N after a residence time of 10 min using the MFI-21.6 analyzer from the company Göttfert analogously to DIN 53 735.

Examples 8-13

The Examples 8-13, which were designed on a semi-industrial scale, were obtained by polycondensation in steel autoclaves which were designed for excess pressure, and heated with a heat exchange oil. In the process, the monomers, their SMA resin and optionally laromin are weighed in the quantities indicated in Table 3.

For the batches with 7 kg product, 500 mL water is added, and for the 45-kg batches, 6 L water is added. The autoclave is closed, nitrogen is introduced, and the temperature is increased to 220°C under stirring. After a pressure of 10 bar has built up, the melt is stirred for 3 h at this temperature and at this pressure. Then the autoclave is opened under nitrogen, so that the excess pressure can be degraded.

After the atmospheric pressure is reached, the temperature is increased to the values indicated in Table 3.

After the completion of the reaction, the autoclave is opened, and the polymer is removed by introducing nitrogen. The strand is drawn through a water bath and granulated. The graft polymers, which are based on caprolactam and aminocaproic acid, are freed of monomer caprolactam by extraction with water. The granulate is dried at 80°C in a vacuum.

To examine the mechanical properties, drawn rods having a thickness of 4 mm of type No. 3 according to DIN 53 455, and for measuring the notch impact resistance, standard small rods 50 x 6 x 4 mm according to DIN 53 453 are manufactured by injection molding. The modulus of elasticity from the traction test is determined according to DIN 53 457.

The results of the tests on the products of Examples 8-13 can be obtained from Tables 4 and 5.

TABLE 2

Example	Als/g	SMA 100		Method				Analytics				End groups	
		$\mu\text{mol/g}$	g	$T/^\circ\text{C}$	t/h	$T/^\circ\text{C}$	t/h	$T/^\circ\text{C}$	mp/ $^\circ\text{C}$	η_{rel}	SMV/Pa.s 122.6 N/270°C	COOH	NH ₂
1	72.6	10	1.1	200	1	270	4	24	180	2.45	1691	63	<5
2	"	20	2.2	"	"	250	"	24	180	1.83	75	137	<5
3	"	30	3.4	"	"	"	"	26	179	1.62	20	151	7
4	"	40	4.5	"	"	"	"	23	177	1.45	<10	256	<5
5	"	50	5.6	220	"	"	"	24	174	1.47	"	310	"
6	"	75	8.4	220	"	"	"	18.5	171	1.31	"	429	"
7	"	100	11.2	"	"	"	"	19	166	1.22	"	500	"

Abbreviations:

ACS	Aminocaproic acid
ALS	Aminolauric acid
CL	Caprolactam
SMA	Styrene-maleic acid anhydride resin
LAR	Laromin C-252
SMV	Melt viscosity

TABLE 3

Example	Recipe							Process			Degassing			
	CL/kg	ACS/kg	ALS/kg	SMA 1000		LAR		Pressure phase			T/°C	t/h	T/°C	t/h
				$\mu\text{mol/g}$	kg	$\mu\text{mol/g}$	kg	T/°C	t/h	p/at				
8	45	0.55	—	15	1.15	—	—	220	3	10	240	3	270	3
9	7.5	—	0.24	15	0.19	—	—	220	3	10	240	3	270	3
10	45	0.52	—	15	1.08	—	—	220	3	10	240	1	270	2
11	7.5	0.24	—	15	0.19	125	152	220	3	10	240	3	270	3
12	—	—	45.00	20	1.44	—	—	220	3	10	270	4	—	—
13	2.6	—	4.00	20	0.20	—	—	220	3	10	240	1	270	4

Abbreviations:

ACS	Aminocaproic acid
ALS	Aminolauric acid
CL	Caprolactam
SMA	Styrene-maleic acid anhydride resin
LAR	Laromin C-252
SMV	Melt viscosity

TABLE 4

Analytics graft polymers industrial scale						
Example	End groups		Solution viscosity	SMV	SCHMP	TG
	COOH	NH ₂				
	$[\mu\text{mol/g}]$		η_{rel}	[Pa.s]	[°C]	[°C]
8	138	12	1.802	51	220	42
9	113	<5	2.195	214	220	44
10	135	13	2.167	174	220	43
11	22	132	1.872	165	222	42
12	147	9	2.120	264	176	20
13	119	10	2.036	60	126	7

TABLE 5

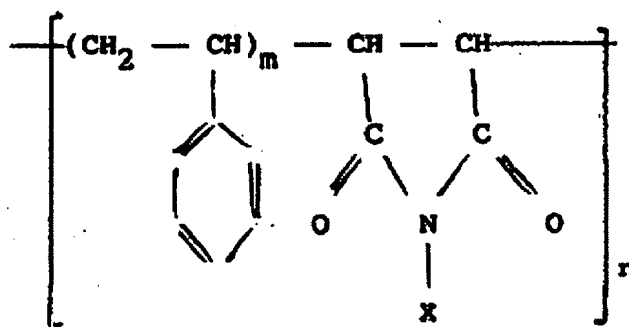
Mechanical properties										
Example	Notch impact resistance		Traction/Tensile E modulus		Yield tension		Yield expansion		Rupture resistance	
	$[\text{KJ/m}^2]/23^\circ\text{C}$		$[\text{N/mm}^2]$		$[\text{N/mm}^2]$		[%]		$[\text{N/mm}^2]$	
	Dry.	Cond.	Dry.	Cond.	Dry.	Cond.	Dry.	Cond.	Dry.	Cond.
8	3	n.d.	—	700	83	30	12	27	59	52
9	3	n.d.	—	1270	85	39	11	45	57	45
10	2	n.d.	—	960	—	43	—	37	89	48
11	2	23	—	1110	—	37	—	39	65	42
12	—	5	—	1470	—	53	—	25	49	48
13	13	n.d.	—	540	48	29	14	35	27	25

Abbreviations

Dry.	Drying
Cond.	Condensation
n.d.	no data

Claims

1. Thermoplastically processable graft polymers, which consist primarily of a styrene-maleinimide base structure unit and polyamino acid chains grafted to it.
2. Graft polymers according to Claim 1, characterized in that the polyamino acid chains, are linked via imide compounds with a styrene/maleinimide base structure unit having the formula I,



(I)

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Where

- m stands for 1-5, and

- n for 3-15, and

- the molecular weight of the base structural unit is 600-9000 g/mol, to the polymer acid units at X.

3. Graft polymers according to Claim 1 or 2, characterized in that the molecular weight is 10,000-100,000 g/mol.

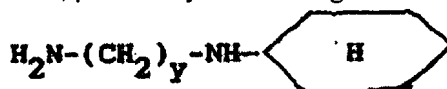
4. Graft polymers according to Claims 1-3, characterized in that m stands for 1-3, and n for 4-8, particularly m for 1-2, and n for 5-7.

5. Graft polymers according to Claims 1-4, characterized in that the polyamino acid chains are built from amino acids and/or lactams, particularly from caprolactam, oenantholactam, laurin lactam, aminoundecanoic acid, aminododecanoic acid, 4-aminomethylbenzoic acid, alone or in combination.

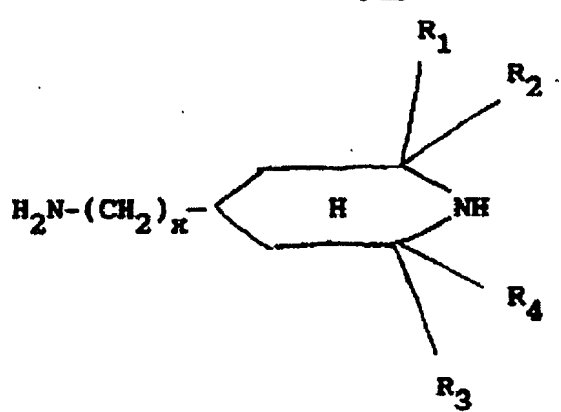
6. Graft polymers according to Claims 1-5, characterized in that the polyamino acid chains consist of polyamide 6, polyamide 11 or polyamide 12 homo- or copolyamide.

7. Graft polymers according to Claims 1-6, characterized in that polyamino chains bear carboxyl end groups which are reacted at least partially with primary amines.

8. Graft polymers according to Claims 1-7, characterized in that the primary amines present alkyl residues with 3-18 carbon atoms, cyclic alkyl residues with 6-18 carbon atoms or aromatic residues with 6-18 carbon atoms, or a sterically hindered second amino function-bearing amine, particularly those having the formula III and/or IV.



(III)



(IV)

wherein X stands for 0-12

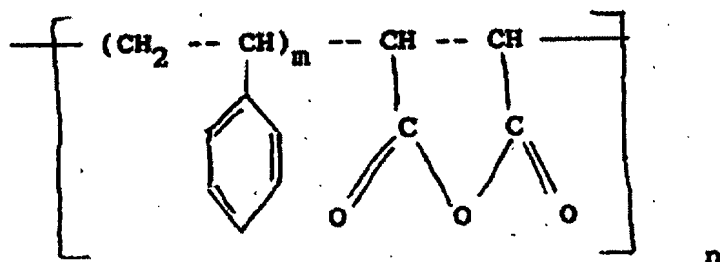
Y for 2-12, particularly 3, and

R1-R4 stand for the same or different alkyl groups with 1-4 carbon atoms, particularly for methyl groups.

/10

9. Graft polymers according to Claims 1-8, characterized in that the polymer composition contains 0.1-15 wt% linear polyamino acid molecules.

10. Method for the manufacture of thermoplastically processed graft polymers according to Claim 1, characterized in that a styrene-maleic acid anhydride resin having the formula (II),



wherein

m stands for 1-5

n for 3-15,

is added to amino acids and/or lactams, the mixture is melted under an inert gas, and, while stirring at temperatures up to 290°C and at the resulting pressure, the polymerization reaction is carried out to reach the desired molecular weight.

11. Method according to Claim 10, characterized in that a monomer and/or dicarboxylic acid is added to the starting monomer in the chain length-regulating mol portion.

12. Method according to Claim 10, characterized in that a monofunctional amine is added to the starting mixture at a maximum mol proportion corresponding to the formula

$$C_A \leq C_{SMA} \eta + 50 \mu\text{mol/g graft polymer},$$

where C_A stands for the concentration of the amine, C_{SMA} for the concentration of the SMA resin (each in $\mu\text{mol/g}$ graft polymer), and n for the number of maleic acid anhydride groups per styrene-maleic acid anhydride molecule.

13. Method according to Claim 10 or 12, characterized in that an amine, which contains, in addition to the condensation-active amino group, a sterically hindered amino group, and particularly an amine having the formula III or IV, is added to the mixture.

14. Use of the thermoplastically processable graft polymers according to Claims 1-13, for the manufacture of mold parts, particularly mold parts having thin walls.